

A Transparent, High Barrier, and High Heat Substrate for Organic Electronics

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Invited Paper

The use of plastic film substrates for organic electronic devices promises to enable new applications, such as flexible displays and conformal lighting, and a new low-cost paradigm through high-volume roll-to-roll fabrication. Unfortunately, presently available substrates cannot yet deliver this promise because of the challenge in achieving the required combination of optical transparency, impermeability to water and oxygen, mechanical flexibility, high-temperature capability, and chemical resistance. Here, we describe the development and performance of a plastic substrate comprising a high heat polycarbonate film combined with a unique transparent coating package that is aimed at meeting this challenge.

Keywords—Flexible display, organic light-emitting devices (OLEDs), permeation barrier, plastic substrate.

I. INTRODUCTION

The promise of organic electronics lies in the potential for building large area electronic devices with much lower cost than possible with conventional silicon-based technology [1]. The main reason for this is that the active layers of the device can be applied using low cost printing techniques that are compatible with high-volume “roll-to-roll” manufacturing. Example low-cost electronic technologies that have been demonstrated include organic light-emitting devices (OLEDs) [2], [3], organic photovoltaic devices [4]–[6], thin-film transistors (TFTs) and TFT arrays using

both organic [7]–[9] and solution-processible inorganic materials [10], [11], and more complicated circuits [12]–[14]. OLEDs represent the most advanced of these technologies as evidenced by the fact that OLED display products are now commercially available. However, these products are still manufactured using predominantly batch-mode conventional semiconductor fabrication processes and so have still not demonstrated the low cost and large area potential of organic electronics. Thus, considerable research effort is being directed toward fabricating OLEDs using printing processes on roll-to-roll compatible, mechanically flexible substrates. A key impediment for this effort is the lack of availability of a mechanically flexible substrate that fulfills all the requirements for a functional OLED. In this paper, we describe progress toward developing such a substrate.

The key requirements for a roll-to-roll compatible plastic OLED substrate are optical transparency, mechanical flexibility, chemical resistance, thermal stability, and impermeability to OLED degradation accelerants such as water and oxygen. Optical transparency is required for the most common “down-emitting” device structure where the transparent electrode is the first device layer deposited onto the substrate. Typical display applications require that the substrate exhibit >90% transmittance over the 400–700 nm visible range. It should be noted that optical transparency is not necessarily required in a substrate used for “up-emitting” OLED architectures, but these approaches face other design constraint and manufacturing integration issues.

Mechanical flexibility is required for roll-to-roll processing and for various envisioned end-use applications such as “roll-up” displays. A typical metric to quantify this is the ability to bend over a 1-in diameter 1000 times. Chemical resistance is required for substrate compatibility with the solvents and chemicals used in organic electronic device fabrication steps. A typical list of the materials that the substrate must be compatible with includes methanol,

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isopropanol, acetone, tetrahydrofuran, n-methylpyrrolidone, ethylacetate, sulfuric acid, glacial acetic acid, hydrogen peroxide, and sodium hydroxide.

Many plastic films can deliver the required combination of transparency, mechanical flexibility, and chemical resistance. However, the additional requirement for temperature stability then limits the choice of plastic film material. High-temperature-stability films are desired mainly for compatibility with high-temperature process steps. Such steps can range from simple drying steps where higher temperature results in faster processing to TFT material deposition where higher temperature results in higher performance. Specific processes have different temperature requirements and/or tradeoffs with temperature. Thus, there is not a consensus among the technical community around a single temperature value requirement for a substrate. However, a useful upper-limit target value is 350 °C as this is currently a lower-limit processing temperature for conventional high-performance α -Si TFTs. At present, no transparent plastic film exists with this level of temperature stability but clearly, as new films are developed which come closer to meeting this goal, more high-performance organic electronic devices and/or applications become possible.

Impermeability to water and oxygen represents the most demanding technical requirement for a roll-to-roll compatible OLED substrate because the active organic materials and electrodes of an OLED degrade in the presence of water and oxygen [15]. Simple calculations suggest that in order to achieve a device lifetime of tens of thousand hours, the substrate must provide a barrier that limits diffusion to less than 10^{-6} g/m²/day and 10^{-5} cc/m²/day for water and oxygen, respectively [16]. This level of hermeticity is beyond the capability of any known plastic film as typical moisture diffusion rates of such materials are in the 1–100 g/m²/day range. For this reason, any plastic film based substrate for use with OLEDs will need to be coupled with some sort of transparent “ultra-high barrier” (UHB) coating to provide the required hermeticity. To date, the most promising mechanically flexible substrate solution that has been proposed consists of a polyethylene terephthalate (PET) film combined with a multilayer UHB coating [17], [18]. The multilayer consists of alternating inorganic and organic layers that collectively are transparent and thin enough to maintain adequate flexibility. Barrier performance in the range of 10^{-6} g/m²/day [19] has been demonstrated and attributed to a mechanism whereby the organic layers decouple pinhole defects in the otherwise-impermeable inorganic layers such that water and oxygen are forced to follow a highly tortuous—and hence slow—diffusion path [20]. OLEDs with reasonable lifetime have recently been demonstrated with this substrate [21].

In spite of the promising performance of the PET substrate, there is still a long way to go in terms of achieving higher temperature stability since, depending on process details, PET is typically limited to 110 °C. In addition, the multilayer nature of the UHB may be susceptible to delamination with repeated mechanical or thermal cycling. Here, we describe an alternative approach to a substrate suitable for OLED processing that addresses some of these

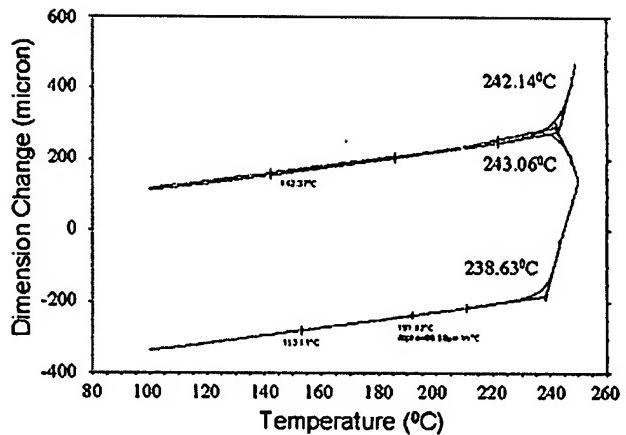


Fig. 1. Thermomechanical analysis performed on uncoated novel high heat polycarbonate film substrate. The temperatures at which one sees dramatic changes in dimensional change rate is a measure for the glass transition temperature.

limitations. The substrate is based on a high-temperature polycarbonate film coupled with a graded rather than a multilayer UHB coating. In this paper, we describe these two components of the substrate individually in the following two sections and then the performance of the combined package in Section IV.

II. HIGH HEAT POLYCARBONATE SUBSTRATE

Commercially available Bisphenol A (BPA) polycarbonate, such as GE’s Lexan polycarbonate resin has a glass transition temperature (T_g) around 150 °C. Higher T_g variants can be made by modifying the monomer. The novel polycarbonate material used in this work has a T_g around 240 °C, as determined by thermomechanical analysis (TMA); see Fig. 1. This novel polycarbonate material has significant advantages for developing high-temperature flexible substrates over other polymeric materials. These advantages include high-temperature process compatibility, high dimensional stability, high optical transparency, smooth surface, and low optical anisotropy. Films with a thickness of 125 μ m were made using this material through a solvent-casting process. Thermal and dimensional stability are critical to flexible organic device fabrication as these properties enable the substrate film to withstand the high-temperature deposition processes required for many device fabrication steps. As received, this polycarbonate film exhibits a shrinkage rate of 700–800 ppm/hr at 200 °C, which is too high for most optoelectronic device fabrication. However, its dimensional stability can be dramatically enhanced by a heat stabilization process. With exposure to a temperature slightly higher than its T_g for a short period of time, the shrinkage rate of this polycarbonate film is reduced to only 25 ppm/hr at 200 °C. The optical clarity of this polycarbonate substrate film is also excellent. Fig. 2 shows that this film is color neutral and has an average light transmittance of 90% in the visible light range.

A wide range of solvents and chemicals can potentially be used during flexible organic device fabrication. One limitation of polycarbonate materials in general is that they exhibit

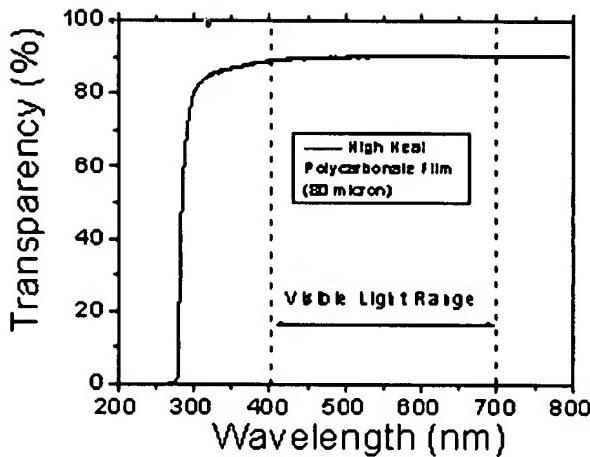


Fig. 2. Transmittance spectrum of uncoated novel high heat polycarbonate film substrate. The average transmittance of this high heat polycarbonate film in visible light range is 90.0%.



Fig. 3. Photographs of a chemical resistance layer coated (left) and uncoated (right) polycarbonate film after exposure for 10 min to acetone. No degradation is observed on the coated substrate.

poor solvent resistance and typically degrade in the presence of common processing chemicals. In order to overcome this, we developed an epoxy-based chemical resistance coating and applied it to both sides of the polycarbonate film. Fig. 3 shows a comparison between a coated and uncoated film when exposed to acetone. One can see that the optical quality of the polycarbonate film is degraded without the coating but effectively protected with the coating. In order to assess this strategy for providing chemical resistance, similar tests were performed with a full range of solvents typically used during organic electronic device fabrication and it was found that the epoxy-based coating protected the polycarbonate in all cases. Another potential issue with polycarbonate relates to dimensional instability due to water uptake since polycarbonate is known to absorb about 0.4% moisture at equilibrium [22]. However, with proper drying procedures, we were able to avoid any detrimental moisture uptake effects during our coating and device fabrication processes. Surface smoothness is another important base film feature because surface roughness can create defects in barrier coatings and electrical shorts in the active OLED. This polycarbonate film has nice surface properties as its average roughness is less than 1 nm and its peak-to-valley roughness is less than 20 nm. Hence, high heat polycarbonate coated with an epoxy-based chemical resistance layer was chosen as the base film for substrate development.

III. UHB COATING

A great amount of literature has been accumulated during the past 20 years on applying vacuum deposited inorganic layers on polymer substrates in order to improve the barrier properties against water vapor and oxygen permeation [23]–[27]. Although bulk inorganics such as a perfect SiO₂ film are effectively impermeable to moisture and oxygen [28], [29], single-layer inorganic barrier coatings only reduce the moisture and oxygen permeation rates by at most two to three orders of magnitude as compared to that through uncoated polymer [20], [25], [26], [30], [31]. The reason for the limited barrier improvement attainable with a single inorganic barrier coating is now well understood to be due to nanometer- to micrometer-size defects in the coating that originate either from the surface roughness of the underlying substrate or from the inorganic coating processing conditions [32]. These defects provide easy pathways for moisture and oxygen diffusion, and thus limit the barrier performance. Evidence of this defect-driven permeation mechanism can be found through studies of permeation rate as a function of inorganic coating thickness. Permeation rate through a defect-free bulk film should exhibit Fickian diffusion and should thus vary inversely with film thickness. However, this is not normally observed for thin-film barrier coatings. Typically, gas permeation rate reduces rapidly by two to three orders of magnitude with increasing coating thickness up to a “critical thickness” of 10–30 nm but, for larger thicknesses, the permeation rate does not decrease further [26]. Thus, regardless of barrier material or deposition method, the best barrier performance achieved so far from a single-layer inorganic coating is several orders of magnitude short of the OLED requirement.

In order to meet the stringent requirements put forth for the design of OLEDs and other organic electronic devices on plastic substrates, a robust coating design should be realized that avoids easy defect pathways for permeation. Multilayer barrier structures comprised of multiple sputter-deposited aluminum oxide inorganic layers separated by polymer multilayer (PML) processed organic layers have demonstrated promising moisture permeation rates in the range of 10^{-6} – 10^{-5} g/m²/day [19], [33], [34]. It is commonly understood that organic layers decouple the defects in the inorganic layers and, thus, prevent the propagation of the defects from one inorganic layer to the other inorganic layers [35]. In other words, the multilayer stack stops defects from propagating in the vertical direction through the coating thickness. A modeling study suggests that this defect decoupling forces a tortuous path for moisture and oxygen diffusion, and thus reduces the permeation rate by several orders of magnitude [20]. Another study suggests that the inorganic–organic multilayer stack leads to higher performance through a transient rather than steady-state phenomenon [36]. Regardless of mechanism, this multilayer barrier stack approach appears to be capable of yielding the required level of performance for OLED applications.

One potential limitation of the multilayer stack approach is that this type of structure tends to suffer from poor adhesion

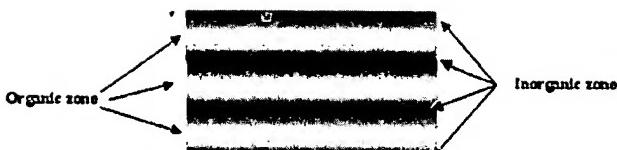


Fig. 4. Schematic of graded inorganic–organic UHB coating.

and delamination, especially during the thermal cycles of the OLED fabrication processes since the inorganic and organic layers have sharp interfaces with weak bonding structure due to the nature of the sputter deposition and PML processes [37], [38]. In order to overcome this, we have developed an alternative graded UHB coating that can effectively stop defects from propagating through the coating thickness. Furthermore, this graded UHB coating is less than $1\text{ }\mu\text{m}$ thick, which is much thinner than that of a typical multilayer barrier stack. According to a simple calculation [39], this reduction in thickness can significantly reduce the effective edge diffusion of water through the organic portion of the barrier coating to be well below $10^{-6}\text{ g/m}^2/\text{day}$. The coating is fabricated using plasma enhanced chemical vapor deposition (PECVD) with a parallel plate capacitively coupled plasma reactor [39]. It consists of a novel, graded single layer made up of inorganic and organic materials as schematically shown in Fig. 4. In this barrier structure, the organic materials effectively decouple defects growing in the thickness direction but, instead of having a sharp interface between inorganic and organic materials, there are “transitional” zones where the coating composition varies continuously from inorganic to organic and vice versa. These “transitional” zones bridge inorganic and organic materials which should result in a single-layer structure with improved mechanical stability and stress relaxation [35], relative to that of multilayer barrier structures.

A. Graded UHB Process Development

There are two base PECVD processes required to fabricate the UHB coating—an inorganic and an organic process. The inorganic process utilizes a combination of silane, ammonia, and oxygen gases to create a material composition ranging between silicon nitride and silicon oxide. The organic process includes a combination of Si-containing organic precursor and Ar gases to create a Si-containing organic material. The inorganic and the organic processes were tailored such that the resulting materials have hardness (inorganic material: $10\text{--}15\text{ GPa}$, organic material: $<1\text{ GPa}$) and elastic modulus (inorganic material: $50\text{--}100\text{ GPa}$, organic material: $<10\text{ GPa}$) similar to those of glass-like materials and thermoplastics, respectively.

A PECVD inorganic film deposited on top of an organic material by nature has $\sim 10\text{ nm}$ of a “transitional” region that exhibits a continuously graded composition between the inorganic and organic material due to ion bombardment [35]. However, the high-energy ion bombardment normally results in a highly stressed film that adversely affects the adhesion of subsequent layers. For instance, an OLED device typically requires the deposition of a transparent conductive

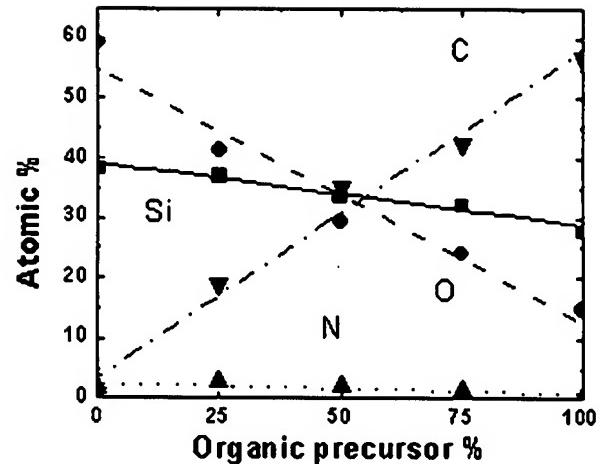


Fig. 5. X-ray photoelectron spectroscopy (XPS) analysis on the coating composition as a function of precursor gas composition.

oxide electrode such as indium–tin–oxide (ITO) on top of the UHB. A low-stress barrier coating is desirable for better adhesion of this layer. Thus, instead of resorting to high-ion bombardment energy, our graded UHB structure is obtained by gradually mixing the inorganic and the organic processes. At constant pressure and radio-frequency (RF) power, each mass flow controller (MFC) for each individual process gas is programmed to achieve continuous compositional changes, while the plasma remains on, in order to achieve a gradual change in the coating composition from inorganic to organic materials and vice versa. For example, if one wants to achieve a coating composition that comprises 90% of inorganic and 10% of organic materials, MFC values for the inorganic and the organic process gases are set at 90% and 10% with respect to their original values, respectively. The thickness of the “transitional” zone is determined by the time to change the precursor gas composition from the inorganic process to the organic process and vice versa. Typically due to the nonlinearity of the plasma process, mixing of precursors for two different processes often results in unexpected coating compositions unless the process conditions are carefully selected. In order to avoid such unexpected compositions, the inorganic and the organic processes were developed at the same pressure and RF power. In addition, the inorganic and the organic processes were engineered to have comparable deposition rates.

In order to ensure that coatings with mixed organic and inorganic compositions could be fabricated by keeping all PECVD process variables constant and only changing precursor gas composition, coatings were made and then analyzed for selected precursor gas combinations. Fig. 5 shows the results of X-ray photoelectron spectroscopy (XPS) analysis of these coatings. For these measurements, the coatings were deposited onto a silicon substrate and a few monolayers of the coating were removed from the top surface by low energy Ar sputtering to eliminate surface contamination effects. Fig. 5 indicates that a linear change in the coating composition can be achieved with a linear change in the precursor gas composition. For example, the carbon concentration is nearly zero when the precursor gas composition is that of the

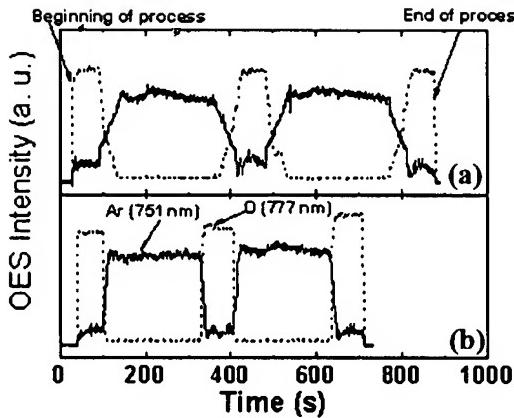


Fig. 6. Time-resolved optical emission spectra for PECVD graded UHB processes with (a) 40 nm and (b) 5 nm of “transitional” zone thickness.

pure inorganic process, and increases linearly with increasing percentage of the organic precursor. Note that the precursor gases for the organic process do not contain oxygen—the oxygen present in the 100% organic process is due to the background from the reactor.

Based on these results, processes were developed to create a single coating with the graded structure depicted in Fig. 4 and varying thickness “transition zones” between inorganic and organic compositions.

Fig. 6(a) and (b) compares the time-resolved optical emission spectra obtained during processing for two different processes with planned transition zones of 40 and 5 nm, respectively. For these measurements, representative emission lines (O at 777 nm for the inorganic process and Ar at 751 nm for the organic process) were selected to monitor the precursor composition change during the UHB deposition. The plasma was on for the whole time at constant pressure and RF power during the UHB process. Fig. 6 clearly indicates that a continuous change in the precursor composition is achieved during both UHB processes. The O emission intensity at 777 nm is high during the inorganic process, and decreases continuously toward a baseline when the fraction of the organic process gases monotonically increases during the “transitional” zone process. At the same time, Ar emission intensity increases continuously.

In order to verify that the desired graded composition coatings were made, depth-profile XPS measurements and cross-sectional transmission electron microscopy (TEM) were performed on the final coatings. The depth profile XPS analysis for the 40-nm transition zone sample shown in Fig. 6(a) is shown in Fig. 7. The data clearly suggests a continuous change in composition as a function of sputter time and hence depth. The XPS depth profiling was accomplished with low energy Ar sputtering. However, there is still the possibility that the apparently continuous change in composition observed may be an artifact caused by chemical changes of the surface induced by mixing or preferential sputtering of the elements [38]. In order to eliminate this interpretation, cross-sectional TEM analysis was performed in parallel on the same coating. Fig. 8 shows representative

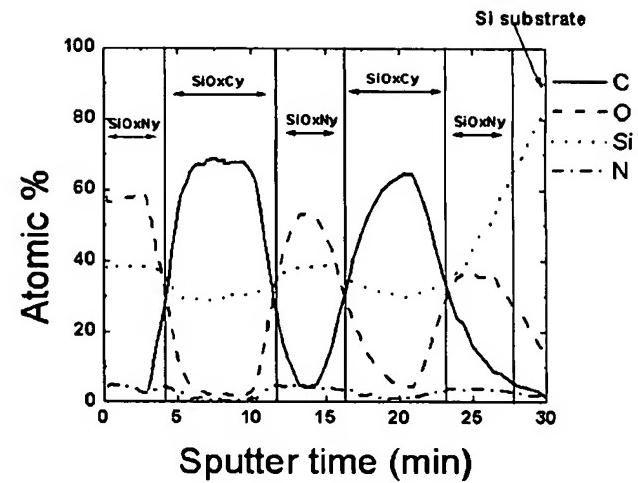


Fig. 7. XPS spectrum for graded inorganic–organic UHB coating.

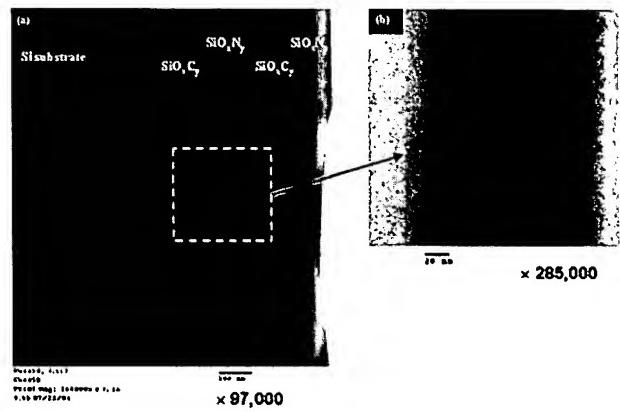


Fig. 8. Cross-section TEM images of graded UHB coating. (a) Low magnification. (b) High magnification.

TEM images. The images clearly show that the coating has a graded structure without a discrete interface.

B. Refractive Index Optimization

Light transmittance and color neutrality are critical requirements for an OLED substrate. One issue with the multilayer approach to a UHB is that the separate organic and inorganic layers typically have different indices of refraction. This leads to multiple reflections and usually additional loss of optical transmission through the multilayer stack. One way around this is to engineer the thickness of the layers to create an interference effect that improves light transmission. Unfortunately, the optimal thicknesses for optical performance are usually not the optimal thicknesses for barrier performance and so overall coating optimization involves an undesirable tradeoff [20], [35].

The single-graded-layer UHB approach can circumvent this tradeoff. In particular, since PECVD is utilized to deposit both inorganic and organic materials, there is a large freedom to tailor film properties such as refractive index through film composition. Thus, it is possible to develop a process that yields the same refractive index for both the organic and inorganic materials and hence avoid multiple reflections. We

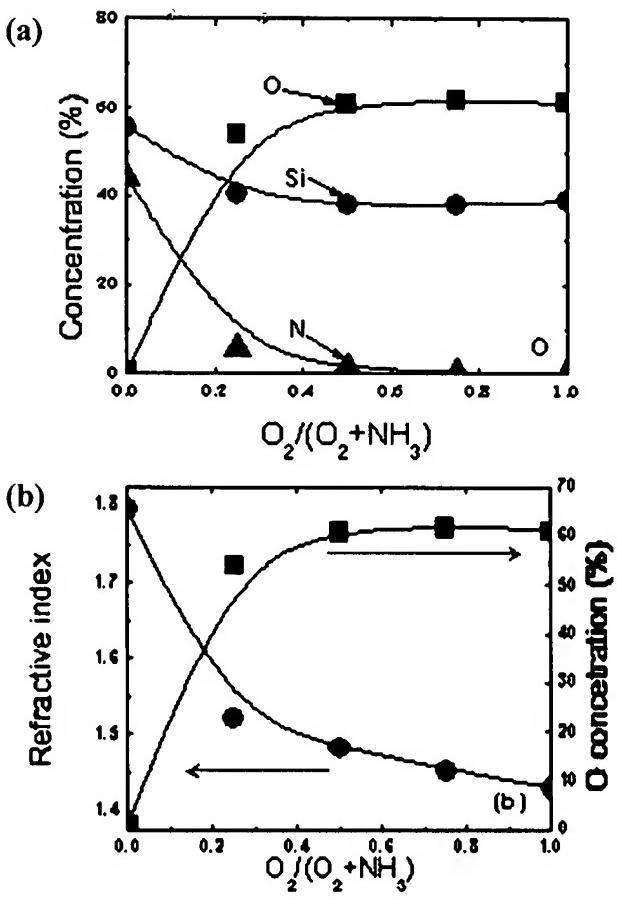


Fig. 9. (a) Coating composition and (b) refractive index at 550 nm for inorganic material as functions of oxygen flow rate.

chose to do this by modifying the inorganic material such that its index matched that of the organic material ($n \sim 1.5$).

Fig. 9 shows the coating composition and refractive index of the inorganic material at 550 nm as a function of oxygen flow rate. The inorganic coatings were deposited on a Si chip at various oxygen flow rates while the total flow rate was maintained at a constant value. The coating composition was obtained using XPS and the refractive index was obtained using spectroscopic ellipsometry. One can see that the atomic oxygen concentration increases rapidly with a small addition of oxygen in the precursor gases, and simultaneously the refractive index dramatically decreases from ~ 1.8 of silicon nitride to ~ 1.5 of silicon oxynitride. Then, the atomic oxygen concentration increases slowly and finally saturates with further increase in oxygen flow rate, and simultaneously the refractive index decreases slowly to ~ 1.4 of silicon oxide.

In order to test the overall optical effect of these inorganic process modifications, graded UHB coatings were deposited onto the polycarbonate films with varying oxygen flow rates for the inorganic process and then the overall light transmittance (%T) through the coated films was collected using a UV-VIS spectrometer. The average %T and the standard deviation of %T were calculated over the wavelength range of 400–700 nm to assess the optical transparency and the amplitude of any interference effects, respectively. Fig. 10 shows these parameters as a function of oxygen flow rate.

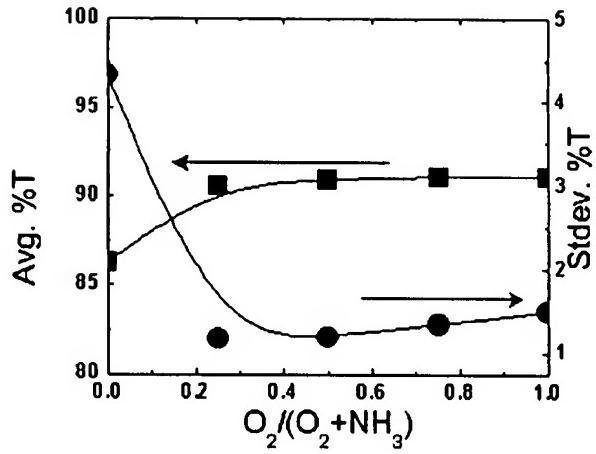


Fig. 10. Average optical transmittance in visible light range and its standard deviation of graded UHB coating as functions of oxygen flow rate used in inorganic coating process.

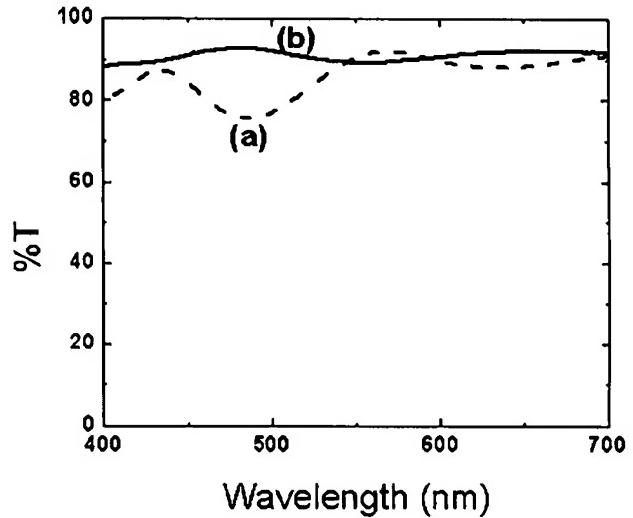


Fig. 11. Optical transmittance spectrum (a) before and (b) after refractive index matching within graded UHB coating.

Note that the average %T is $\sim 86\%$ when the UHB coating includes silicon nitride as an inorganic material, but it increases to above 90% as the oxygen flow rate in the inorganic process increases. One can also see that the amplitude of interference is at a minimum when the oxygen flow fraction is ~ 0.2 —presumably where the refractive index of the inorganic material matches that of the organic material. Fig. 11 compares the complete %T spectra through two distinct graded UHB coatings: (a) silicon nitride as the base inorganic material (oxygen flow fraction of 0), and (b) silicon oxynitride as the base inorganic material (oxygen flow fraction of 0.25). One can see that with the given silicon oxynitride as the base inorganic material, the single-layer graded barrier coating on the polycarbonate substrate indeed has higher overall transmission and greatly minimized interference fringes relative to that with silicon nitride as the base inorganic material. This demonstrates that highly transparent and essentially color-neutral barrier coatings can be made with our single-layer graded approach to a UHB.

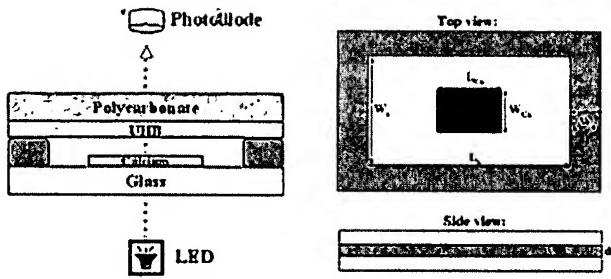


Fig. 12. Illustration of the calcium corrosion test setup and the test cell geometry.

C. UHB Performance

One major obstacle in the development of a barrier enhanced plastic substrate is the lack of a readily available measurement system for water vapor transmission rate in the 10^{-5} – 10^{-6} g/m²/day range. Thus, custom-built measuring systems based on the reaction of calcium with water are typically used to assess the hermeticity of UHB coatings [40], [41]. The schematic of a calcium cell, the measurement system, and the cell geometry utilized for our tests is shown in Fig. 12. Calcium is evaporated onto a glass slide and then the test substrate is attached to the slide to cover the exposed calcium. The attachment is made with a perimeter seal outside of the calcium region. As the water vapor permeates through the substrate and/or the edge perimeter seal, or is being released from any internal sources (e.g., residual moisture in adhesive), it reacts with calcium inside the cell and the calcium layer becomes thinner and more transparent as a function of time. Since the optical density (OD) of a film is proportional to its thickness, we can then calculate the WVTR via the following equation:

$$\text{WVTR} = -2A \frac{M[\text{H}_2\text{O}]}{M[\text{Ca}]} \rho_{\text{Ca}} \frac{L_{\text{Ca}} \cdot W_{\text{Ca}}}{L_s \cdot W_s} \frac{d(\text{OD})}{dt} \quad (1)$$

where A is the scaling factor between calcium thickness and OD, $M[\text{H}_2\text{O}]$, and $M[\text{Ca}]$ are the molar masses of water and Ca with values of 18 and 40.1 amu, respectively, ρ_{Ca} is the density of calcium, L_{Ca} and W_{Ca} are the length and width of the deposited Ca, L_s and W_s are the length and width of the permeation area defined by the interior boundary of the edge perimeter seal (Fig. 12), and $d(\text{OD})/dt$ is the slope of the measured optical absorbance versus time. Details of this testing method are described elsewhere [39].

Several graded UHB samples and reference cells with a glass test sample rather than a UHB-coated plastic sample were prepared and tested with this method at 23 °C and 50% relative humidity (RH). Fig. 13 shows the OD versus time plots for a representative graded UHB and glass/glass reference sample. From these data, WVTR values of $1.7(\pm 0.5) \times 10^{-5}$ g/m²/day for the UHB and $6.8(\pm 0.1) \times 10^{-6}$ g/m²/day for the glass/glass reference cell were calculated using (1). To date, the various graded UHB coatings made in our laboratory span a range from 5×10^{-6} to 5×10^{-5} g/m²/day with glass/glass reference cells reading from 1×10^{-6} to 1×10^{-5} g/m²/day under

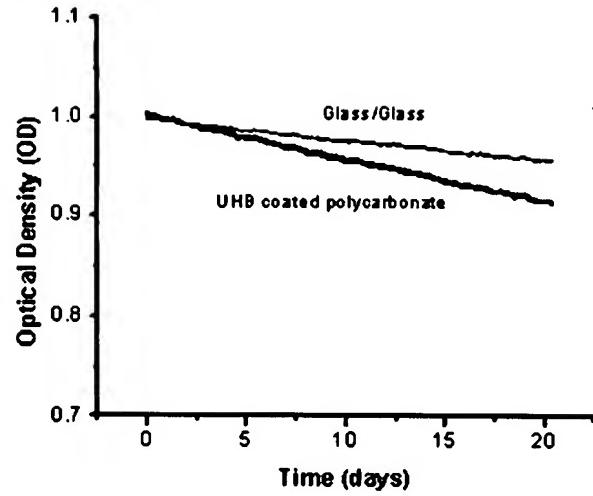


Fig. 13. Optical density versus time plots for UHB and glass/glass reference cells, obtained from the calcium corrosion test.

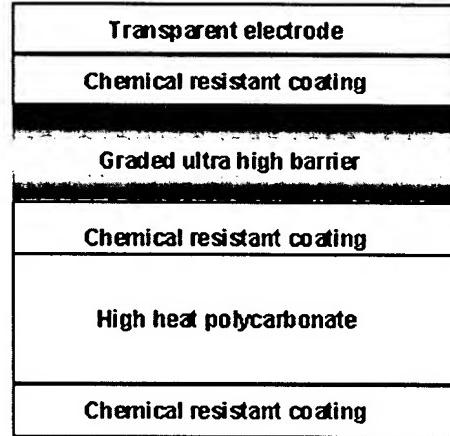


Fig. 14. High heat polycarbonate film with transparent coating package that meets the stringent requirements for application in flexible organic electronics.

these test condition. This is within the range of interest for OLED applications.

IV. COMPLETE SUBSTRATE PACKAGE

In order to demonstrate a complete substrate package for organic electronic device fabrication, all the components described above—the polycarbonate film, the chemical resistance layers, and the single-layer UHB coating—were integrated together. In addition, a layer of indium-tin-oxide was sputtered onto the top of the substrate as this is the typical starting point for OLED manufacturers. Fig. 14 schematically depicts the integrated package. After fabrication of this total package, a full battery of tests including Ca corrosion tests for WVTR, four-point probe measurements for the ITO sheet resistance, UV-VIS analysis for the optical transparency, the ASTM3359 method for adhesion, TMA for dimensional stability, optical profilometry for the surface roughness, and bend tests for mechanical flexibility were performed. The results of this comprehensive evaluation are summarized in Table 1.

Table 1
Comprehensive Coating Package Performance of GE Plastic
OLED Substrate

	GE Performance
WVTR	$5 \times 10^{-6} - 5 \times 10^{-5}$ g/m ² /day
Chemical Resistance	Resistant to commonly used acid, alkali, and solvent
ITO sheet resistance	40 Ω/Sq
Optical Transparency	82 %
Mechanical Flexibility	Bendable around 1" diameter.
Thermo-Mechanical Stability	Sustain 200°C for 1 hr
Adhesion	4B
Thermal dimension stability	Shrinks at 4 ppm/hr at 150°C
Average surface roughness	0.6 nm

The properties depicted in Table 1 are all quite promising for organic electronic device fabrication. However, the final proof of compatibility with OLED processing requires the actual fabrication of a device. Many unanticipated issues such as the presence of particles, handling methods, resistance to a certain set of solvents, stability during high-temperature steps, the effect of mechanical stress due to sealing, performance of the transparent conductor, shelf life, etc. tend to surface during device fabrication. In order to test for these, two-layer polymer OLEDs consisting of PEDOT/PSS [poly(ethylenedioxythiopene)/polysulfonated styrene] as a hole transport layer and a polyfluorene-based light-emitting polymer (LEP) layer were fabricated with our substrate package as the bottom electrode. A series connected architecture described elsewhere [39] was employed to enable a large emitting area. In particular, ten devices consisting of eight series-connected elements, each with area 1.95 cm^2 , were fabricated on a $15 \text{ cm} \times 15 \text{ cm}$ substrate. Fabrication was accomplished using the fairly standard procedure described below.

In order to enable device fabrication using conventional batch processing tools, the substrate films were first affixed to 3-mm-wide $15 \text{ cm} \times 15 \text{ cm}$ square titanium frames by means of double-sided Kapton polyimide tape. The affixed film was cleaned with isopropanol, then a 10-min dwell in an aqueous detergent (Alconox) with ultrasonic agitation, followed by water rinsing and drying.

ITO patterning was accomplished using a photoresist and immersion etching. The photoresist (AZ1512) was applied by means of spin coating and baked for 10 min at 110 °C, producing a film $1 \mu\text{m}$ thick. The positive photoresist was imaged through a glass mask using a UV collimated light source for 15 s. The image was developed at room temperature for 1 min using OCG 809 (2:1). Following a water rinse and drying, the exposed ITO was removed by immersion for 5 min in a 45 °C solution of 10/10/1 hydrochloric acid/water/nitric acid. The sample was rinsed with water, dried, and the photoresist removed by immersion in acetone. Residual materials were removed by a 10 min dwell in an aqueous detergent (Alconox) with ultrasonic agitation, followed by water rinsing and drying.

The active device layers were deposited by means of spin coating. In particular, an aqueous coating of PEDOT/PSS (Baytron P VP CH 8000 from H.C. Stark) was spin coated and baked at 110 °C to produce a film of 50 nm thickness.

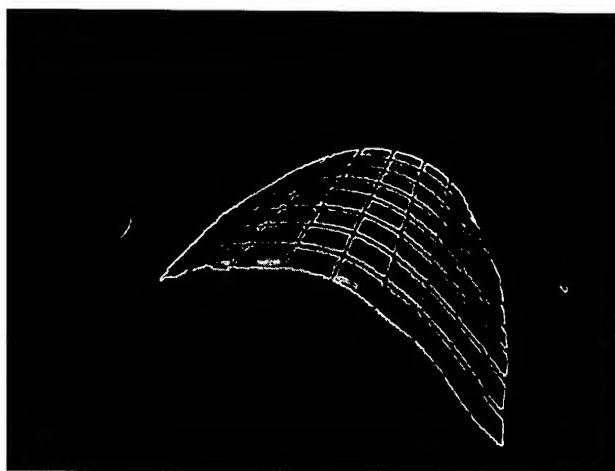


Fig. 15. 15-cm square flexible OLED on high heat polycarbonate substrate with graded UHB.

The LEP layer was fabricated using a solution of LUMATION¹ 1304 in xylene. After spincoating and a 10 min bake on a hot plate, a 70-nm-thick LEP layer was produced. A bi-layer cathode made up of NaF and aluminum was then evaporated onto the films through a stainless steel mask. Finally, the devices were encapsulated with a 100-μm-thick foil of aluminum coated with adhesive inside a glove box. The samples were then removed from the glove box for testing.

Fig. 15 provides a picture of the resulting substrate being bent with all devices turned on at a brightness of $\sim 1000 \text{ cd/m}^2$. At this brightness, the efficiency, as measured in an integrating sphere, is 8 cd/A. This is comparable to that expected for this LEP material [42]. It thus appears that our polycarbonate/graded UHB substrate package is compatible with a polymer-based OLED fabrication process. Efforts are ongoing to assess the detailed performance characteristics of OLEDs made with this substrate as a function of time and environmental conditions.

V. CONCLUSION

We have described the development of a transparent plastic substrate technology that provides the high hermeticity that is expected to be required for many organic electronic devices. The key features of this technology are a polycarbonate film with high-temperature capability and a novel single-graded layer UHB coating that can be tuned for refractive index matching. Simple OLEDs were made on this substrate to demonstrate its compatibility with at least one organic electronic device fabrication technology. In order to further develop the technology, efforts need to be placed in optimizing the substrate for all the possible variants of OLED, passive and active matrix backplane, and other organic electronic device fabrication processes. It should be noted that the performance of the underlying plastic film and of the graded UHB coating are not highly coupled to each other and so separate optimization is possible. Thus, if a new transparent polycarbonate or other polymer film with higher temperature capability is developed, it should

¹LUMATION is a trademark of The Dow Chemical Company.

be possible to apply the graded UHB coating concept with minimal adjustment. This increases the possibility that plastic substrate technologies will be developed for even the most demanding organic electronic device applications.

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REFERENCES

- [1] S. R. Forrest, "The path to ubiquitous and low-cost organic electronic appliances on plastic," *Nature*, vol. 428, pp. 911–918, Apr. 2004.
- [2] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, and W. R. Salaneck, "Electroluminescence in conjugated polymers," *Nature*, vol. 397, pp. 121–128, Jan. 1999.
- [3] S. R. Forrest, "Active optoelectronics using thin-film organic semiconductors," *IEEE J. Sel. Topics Quantum Electron.*, vol. 6, no. 6, pp. 1072–1083, Nov.–Dec. 2000.
- [4] C. W. Tang, "Two-layer organic photovoltaic cell," *Appl. Phys. Lett.*, vol. 48, pp. 183–185, Jan. 1986.
- [5] G. Yu, J. Gao, J. Hummelen, F. Wudl, and A. J. Heeger, "Polymer photovoltaic cells: Enhanced efficiencies via a network of internal donor-acceptor heterojunctions," *Science*, vol. 270, pp. 1789–1791, Dec. 1995.
- [6] J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, and A. B. Holmes, "Efficient photodiodes from interpenetrating polymer networks," *Nature*, vol. 376, pp. 498–500, Aug. 1995.
- [7] A. J. Lovinger and L. J. Rothberg, "Electrically active organic and polymeric materials for thin-film-transistor technologies," *J. Mater. Res.*, vol. 11, p. 1581, Sep. 1996.
- [8] J. A. Rogers, Z. Bao, K. Baldwin, A. Dodabalapur, B. Crone, V. R. Raju, V. Kuck, H. Katz, K. Amundson, J. Ewing, and P. Drzaic, "Paper-like electronic displays: Large area, rubber stamped plastic sheets of electronics and microencapsulated electrophoretic inks," *Proc. Nat. Acad. Sci.*, vol. 98, pp. 4835–4840, 2001.
- [9] E. S. Snow, J. P. Novak, P. M. Campbell, and D. Park, "Random networks of carbon nanotubes as an electronic material," *Appl. Phys. Lett.*, vol. 82, pp. 2145–2147, Mar. 2003.
- [10] X. Duan, C. Niu, V. Sahl, J. Chen, J. W. Parce, S. Empedocles, and J. L. Goldman, "High-performance thin-film transistors using semiconductor nanowires and nanoribbons," *Nature*, vol. 425, pp. 274–278, Sep. 2003.
- [11] D. B. Mitzi, L. L. Kosbar, C. E. Murray, M. Copel, and A. Afzali, "High-mobility ultrathin semiconducting films prepared by spin coating," *Nature*, vol. 428, pp. 299–302, Mar. 2004.
- [12] B. K. Crone, A. Dodabalapur, R. Saraphkar, A. Gelperin, H. E. Katz, and Z. Bao, "Organic oscillator and adaptive amplifier circuits for chemical vapor sensing," *J. Appl. Phys.*, vol. 91, pp. 10 140–10 146, Jun. 2002.
- [13] W. Fix, A. Ullmann, J. Ficker, and W. Clemens, "Fast polymer integrated circuits," *Appl. Phys. Lett.*, vol. 81, pp. 1735–1737, Aug. 2002.
- [14] G. Gelinck, H. E. A. Huitema, E. V. Veenendaal, E. Cantatore, L. Schrijnemakers, J. B. P. H. Van Der Putten, T. C. T. Geuns, M. Beenhakkers, J. B. Giesbers, B. Huisman, E. J. Meijer, E. M. Benito, F. J. Touwslager, A. W. Marsman, B. J. E. Van Rens, and D. M. De Leeuw, "Flexible active-matrix displays and shift registers based on solution-processed organic transistors," *Nature Mater.*, vol. 3, pp. 106–110, Feb. 2004.
- [15] J. K. Mahon, J. J. Brown, T. X. Zhou, P. E. Burrows, and S. R. Forrest, "Requirements of flexible substrates for organic light emitting devices in flat panel display applications," *Soc. Vacuum Coat.*, vol. 505/856–7188, pp. 456–459, 1999.
- [16] P. E. Burrows, G. L. Graff, M. E. Gross, P. M. Martin, M. Hall, E. Mast, C. Bonham, W. Bennett, L. Michalski, M. Weaver, J. J. Brown, D. Fogarty, and L. S. Sapochak, "Gas permeation and lifetime tests on polymer-based barrier coatings," *Proc. SPIE—Int. Soc. Opt. Eng.*, vol. 4105, pp. 75–83, 2001.
- [17] J. D. Affinito, M. E. Gross, C. A. Coronado, G. L. Graff, E. N. Greenwell, and P. M. Martin, "A new method for fabricating transparent barrier layers," *Thin Solid Films*, vol. 290–291, pp. 63–67, Dec. 1996.
- [18] H. C. Langowski, A. Melzer, and D. Schubert, "Ultra high barrier layers for technical applications," in *45th Annu. Technical Conf. Proc. Society of Vacuum Coaters*, 2002, pp. 471–475.
- [19] M. S. Weaver, L. A. Michalski, K. Rajan, M. A. Rothman, J. A. Silvermail, J. J. Brown, P. E. Burrows, G. L. Graff, M. E. Gross, P. M. Martin, M. Hall, E. Mast, C. Bonham, W. Bennett, and M. Zumhoff, "Organic light-emitting devices with extended operating lifetimes on plastic substrates," *Appl. Phys. Lett.*, vol. 81, no. 16, pp. 2929–2931, Oct. 2002.
- [20] M. Schaeppkens, T. W. Kim, A. G. Erlat, M. Yan, K. W. Flanagan, C. M. Heller, and P. McConahey, "Ultrahigh barrier coating deposition on polycarbonate substrates," *J. Vac. Sci. Technol. A*, vol. 22, no. 4, pp. 1716–1722, Jul. 2004.
- [21] A. Chwang, M. A. Rothman, S. Y. Mao, R. H. Hewitt, M. S. Weaver, J. A. Silvermail, K. Rajan, M. Hack, J. J. Brown, X. Chu, L. Moro, T. Krajewski, and N. Rutherford, "Thin film encapsulated flexible organic electroluminescent displays," *Appl. Phys. Lett.*, vol. 83, no. 3, pp. 413–415, Jul. 2003.
- [22] W. A. MacDonald, "Engineered films for display technologies," *J. Mater. Chem.*, vol. 14, pp. 4–10, 2004.
- [23] H. Chatman, "Oxygen diffusion barrier properties of transparent oxide coatings on polymeric substrates," *Surf. Coat. Technol.*, vol. 78, pp. 1–9, Jan. 1996.
- [24] W. Decker and B. M. Henry, "Basic principals of thin barrier coatings," in *45th Annu. Soc. Vacuum Coaters Technical Conf.*, 2002, p. 492.
- [25] A. S. da Silva Sobrinho, M. Latreche, G. Czeremuszkin, J. E. Klemberg-Sapieha, and M. R. Wertheimer, "Transparent barrier coatings on polyethylene terephthalate by single- and dual-frequency plasma-enhanced chemical vapor deposition," *J. Vac. Sci. Technol. A*, vol. 16, pp. 3190–3198, Nov. 1998.
- [26] A. S. da Silva Sobrinho, G. Czeremuszkin, M. Latreche, and M. R. Wertheimer, "Defect-permeation correlation for ultrathin transparent barrier coatings on polymers," *J. Vac. Sci. Technol. A*, vol. 18, pp. 149–157, 2000.
- [27] A. G. Erlat, R. J. Spontak, R. P. Clarke, T. C. Robinson, P. D. Haaland, Y. Tropsha, N. G. Harvey, and E. A. Vogler, "SiO_x gas barrier coatings on polymer substrates: Morphology and gas transport considerations," *J. Phys. Chem. B*, vol. 103, pp. 6047–6055, 1999.
- [28] R. M. Barrer, *Diffusion in and Through Solids*. New York: Cambridge Univ. Press, 1941.
- [29] B. E. Deal and A. S. Grove, "General relationship for the thermal oxidation of silicon," *J. Appl. Phys.*, vol. 36, pp. 3770–3778, Dec. 1965.
- [30] E. H. H. Jamieson and A. H. Windle, "Structure and oxygen-barrier properties of metallized polymer film," *J. Mater. Sci.*, vol. 18, pp. 64–80, Jan. 1983.
- [31] Y. G. Tropsha and N. G. Harvey, "Activated rate theory treatment of oxygen and water transport through silicon oxide/poly(ethylene terephthalate) composite barrier structures," *J. Phys. Chem. B*, vol. 101, pp. 2259–2266, 1997.
- [32] A. P. Roberts, B. M. Henry, A. P. Sutton, C. R. M. Grovenor, G. A. D. Briggs, T. Miyamoto, M. Kano, Y. Tsukahara, and M. Yanaka, "Gas permeation in silicon-oxide/polymer (SiO_x/PET) barrier films: Role of the oxide lattice, nano-defects and macro-defects," *J. Membrane Sci.*, vol. 208, pp. 75–88, Oct. 2002.
- [33] G. Nisato, M. Kuilder, P. Bouter, L. Moro, O. Philips, and N. Rutherford, "Thin-film encapsulation for OLEDs: Evaluation of multilayer barriers using the Ca test," in *Soc. Information Display, 2003 Int. Symp. Dig. Tech. Papers*, vol. XXXIV, p. P-88.
- [34] L. Moro, T. A. Krajewski, N. M. Rutherford, O. Philips, R. J. Visser, M. E. Gross, W. D. Bennett, and G. L. Graff, "Integrated encapsulation of bottom and top emission OLED displays," *Proc. SPIE—Int. Soc. Opt. Eng.*, vol. 5214, pp. 83–93, 2004.
- [35] J. S. Lewis and M. S. Weaver, "Thin-film permeation-barrier technology for flexible organic light-emitting devices," *IEEE J. Sel. Topics Quantum Electron.*, vol. 10, no. 1, pp. 45–57, Jan.–Feb. 2004.
- [36] G. L. Graff, R. E. Williford, and P. E. Burrows, "Mechanisms of vapor permeation through multilayer barrier films: Lag time versus equilibrium permeation," *J. Appl. Phys.*, vol. 96, pp. 1840–1849, Aug. 2004.
- [37] E. H. Nicollian and J. R. Brews, *MOS Physics and Technology*. New York: Wiley, ch. 16.

- [38] A. S. da Silva Sobrinho,² N. Schuhler, J. E. Klemberg-Sapieha, M. R. Wertheimer, M. Andrews, and S. C. Gujrathi, "Plasma-deposited silicon oxide and silicon nitride films on poly(ethylene terephthalate): A multitechnique study of the interphase regions," *J. Vac. Sci. Technol. A*, vol. 16, pp. 2021–2030, 1998.
- [39] A. G. Erlat, M. Schaeckens, T. W. Kim, C. M. Heller, M. Yan, and P. McConnelee, "Ultra-high barrier coatings on polymer substrates for flexible optoelectronics: Water vapor transport and measurement systems," in *47th Annu. Technical Conf. Proc. Soc. Vacuum Coaters*, 2004, pp. 654–663.
- [40] G. Nisato, P. C. P. Bouten, P. J. Slinkerkeer, W. D. Bennet, G. L. Graff, N. Rutherford, and L. Wiese, *Asia Display/IDW'01 Proc.*, 2001.
- [41] P. O. Nilsson and G. Forsell, "Optical properties of calcium," *Phys. Rev. B, Condens. Matter*, vol. 16, pp. 3352–3358, 1977.
- [42] *LUMATION Green 1300 Series LEP Data Sheets*, The Dow Chemical Company.

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